



Announcements

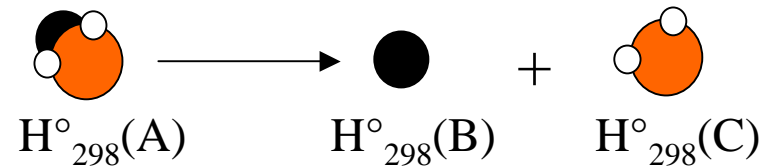
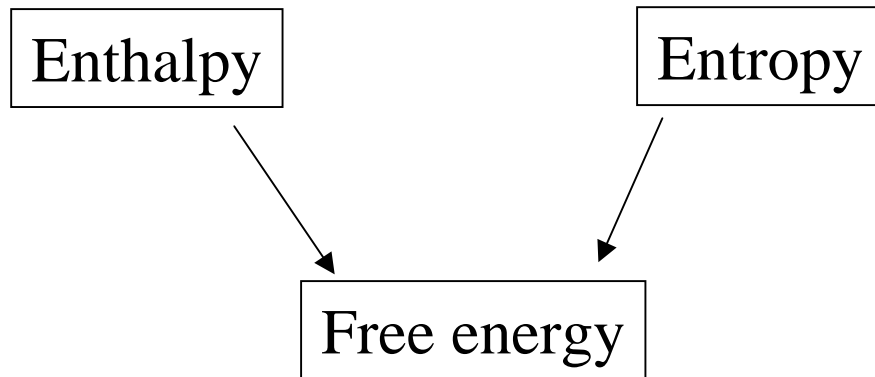
Remember: First exam is next Wednesday!

I will post links to practice problems and exams shortly.
See announcements for possible extra hours etc.

I will not be here Friday. But I will be in during select hours
on the weekend and next week.

The elements of change

What makes a reaction spontaneous?



$$\Delta H = H(B) + H(C) - H(A)$$

$$\Delta S > 0$$

What makes a reaction actually happen?

Molecular Detail, Transport and Kinetics!



The elements of change

We know from last time that

$\Delta H < 0$	exothermic reaction	(combustion)
$\Delta H = 0$	thermoneutral reaction	(ideal gas expansion into a vacuum)
$\Delta H > 0$	endothermic reaction	(ice melting at 25°C)

We tend to think that processes which decrease energy occur spontaneously.

But what about endothermic reactions?

Something's missing!



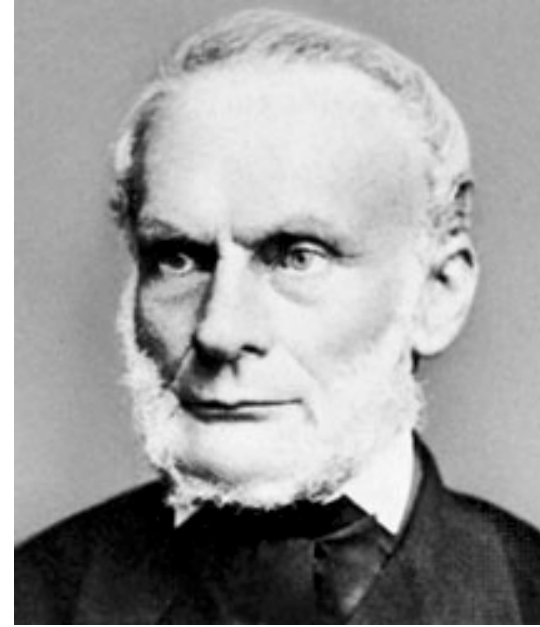
What will make a steam engine go?

How much of the heat put in at high temperature can be converted to work?

Can two engines with the same temperature difference drive one another?

What does entropy have to do with it?

Murphy's law and the heat death of the universe!



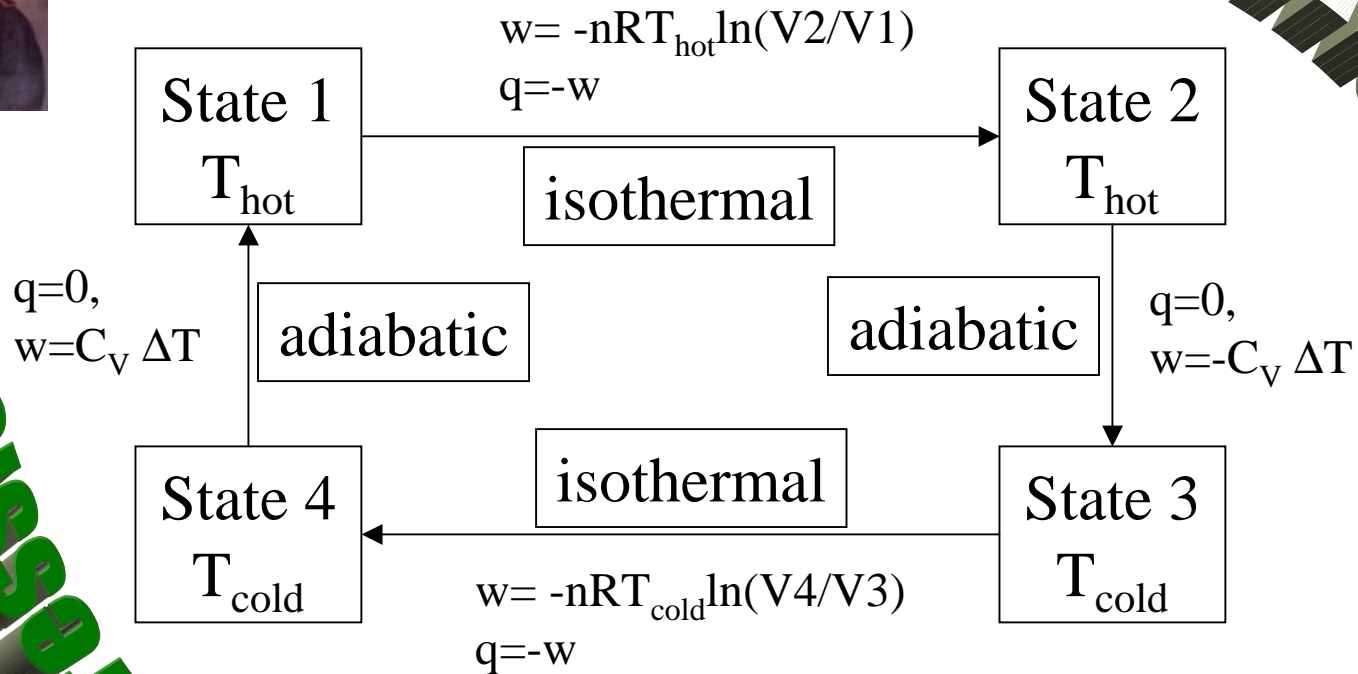
Clausius

b. Jan. 2, 1822, Prussia

d. Aug. 24, 1888, Bonn

"Heat cannot of itself pass from a colder to a hotter body."

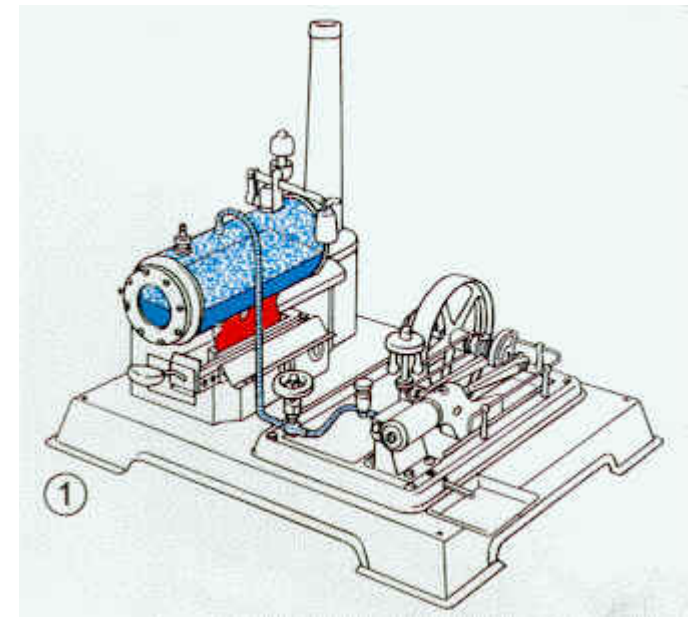
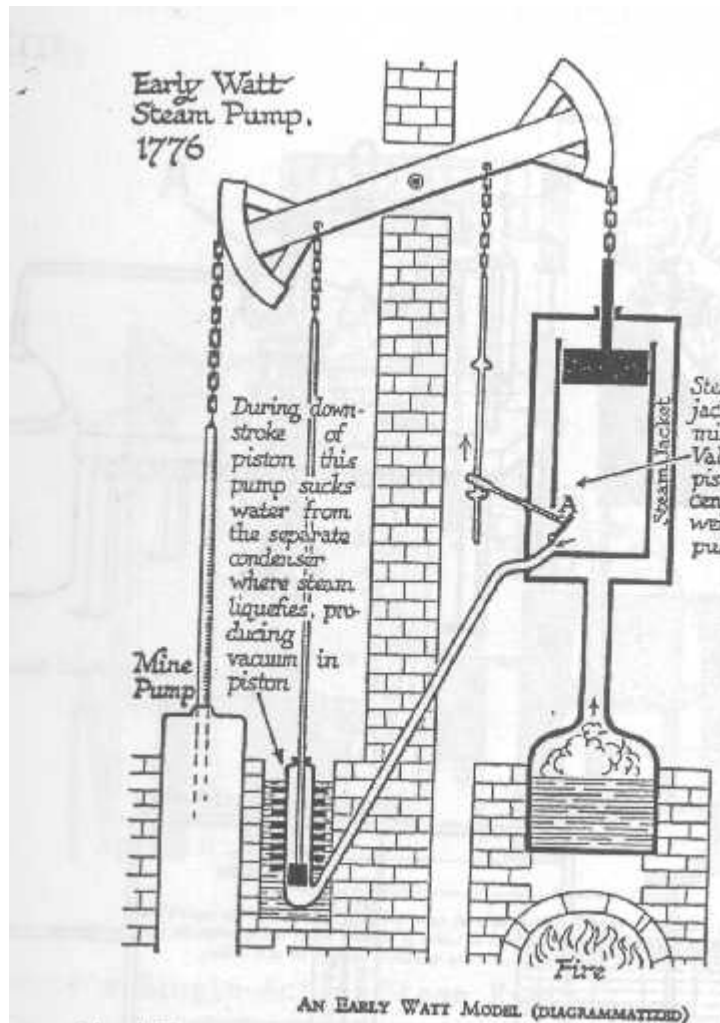
The Carnot Cycle



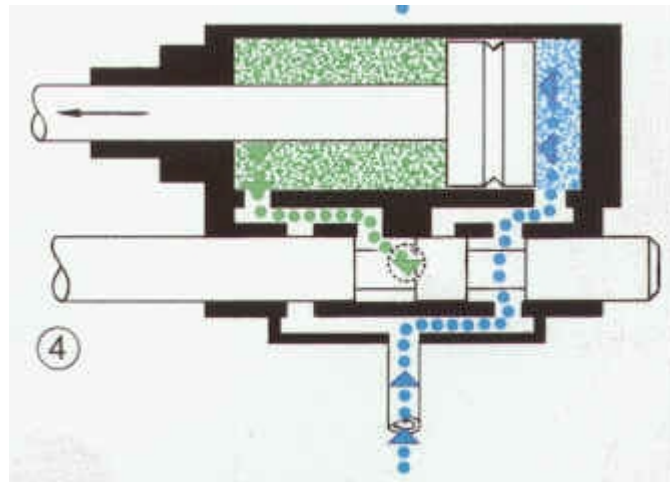
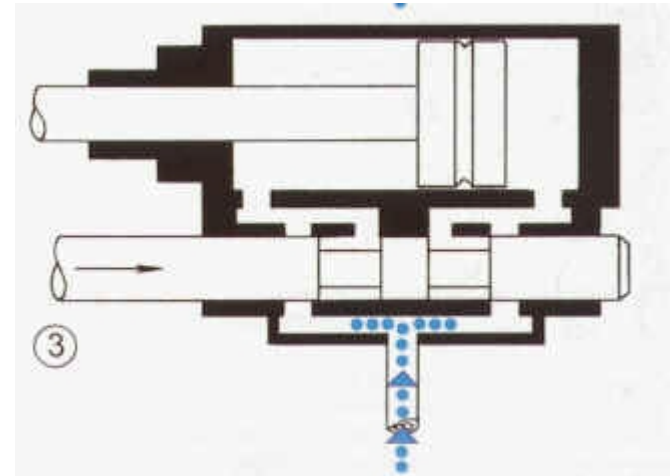
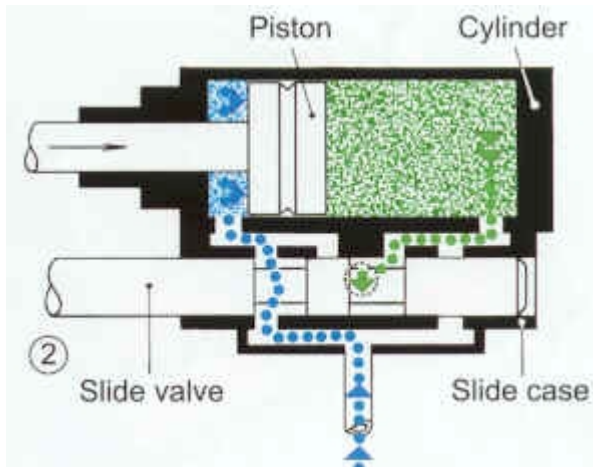
Expansion

Compression

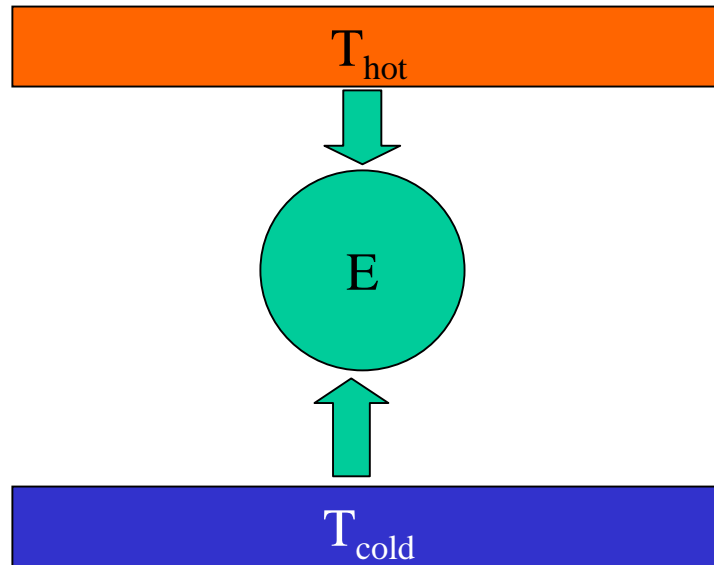
The Carnot Cycle: Engine Schematic



The Carnot Cycle: Engine Schematic



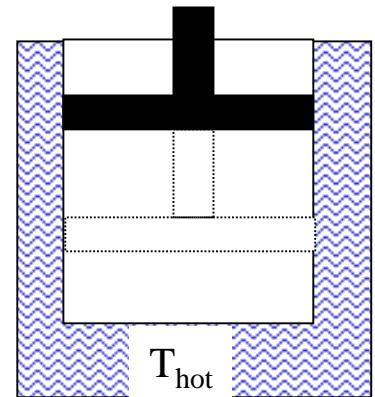
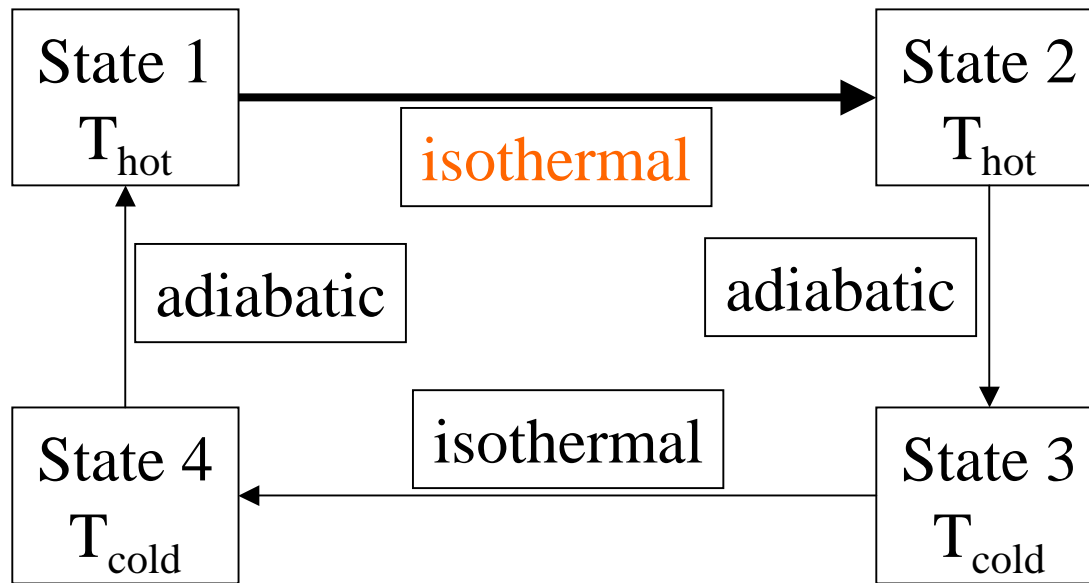
The Carnot Cycle: Another diagram



The engine operates between two reservoirs to and from which heat can be transferred.

We put heat into the system from the hot reservoir and heat is expelled into the cold reservoir.

The Carnot Cycle: Step 1



Heat converted to work!

Isothermal *reversible* Expansion:

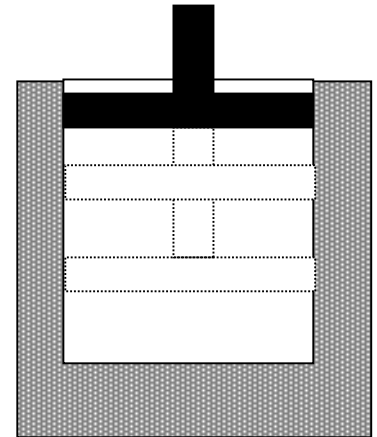
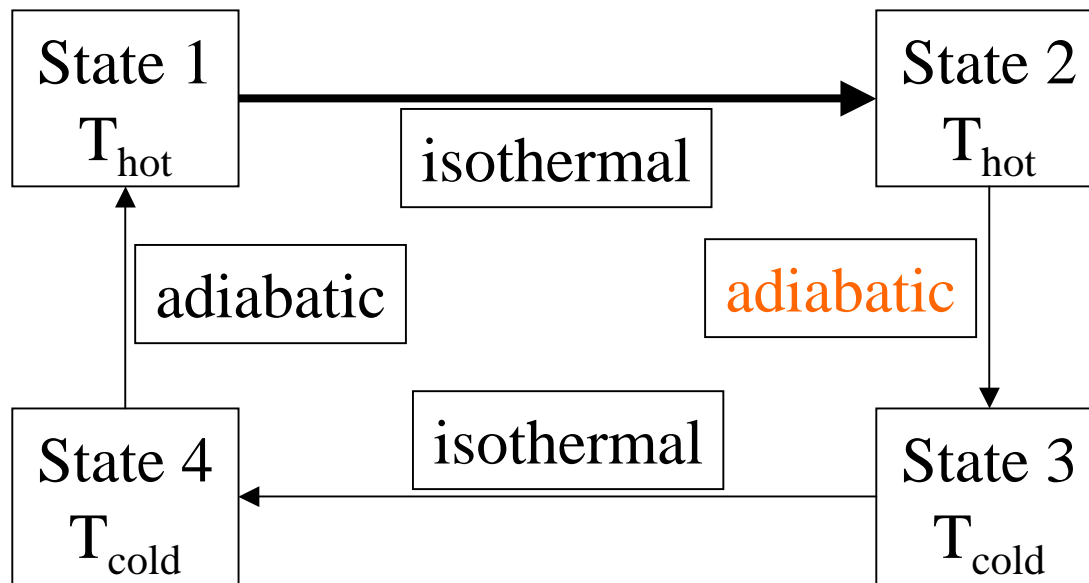
$$\Delta E = 0$$

Energy of an ideal gas depends only on temperature

$$w = - \int_{V_1}^{V_2} P dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$q = -w$$

The Carnot Cycle: Step 2



Energy lost to expansion

Isothermal *reversible* Expansion:

$$q=0$$

No heat transferred in adiabatic process

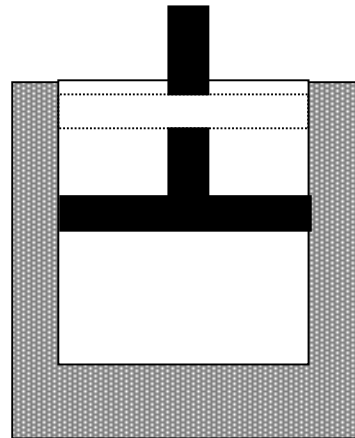
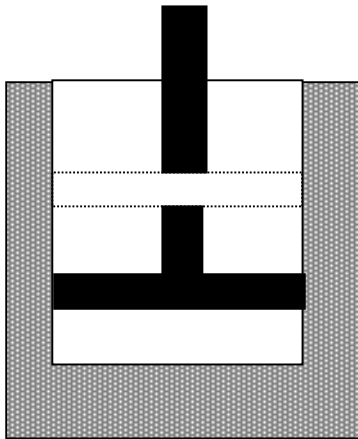
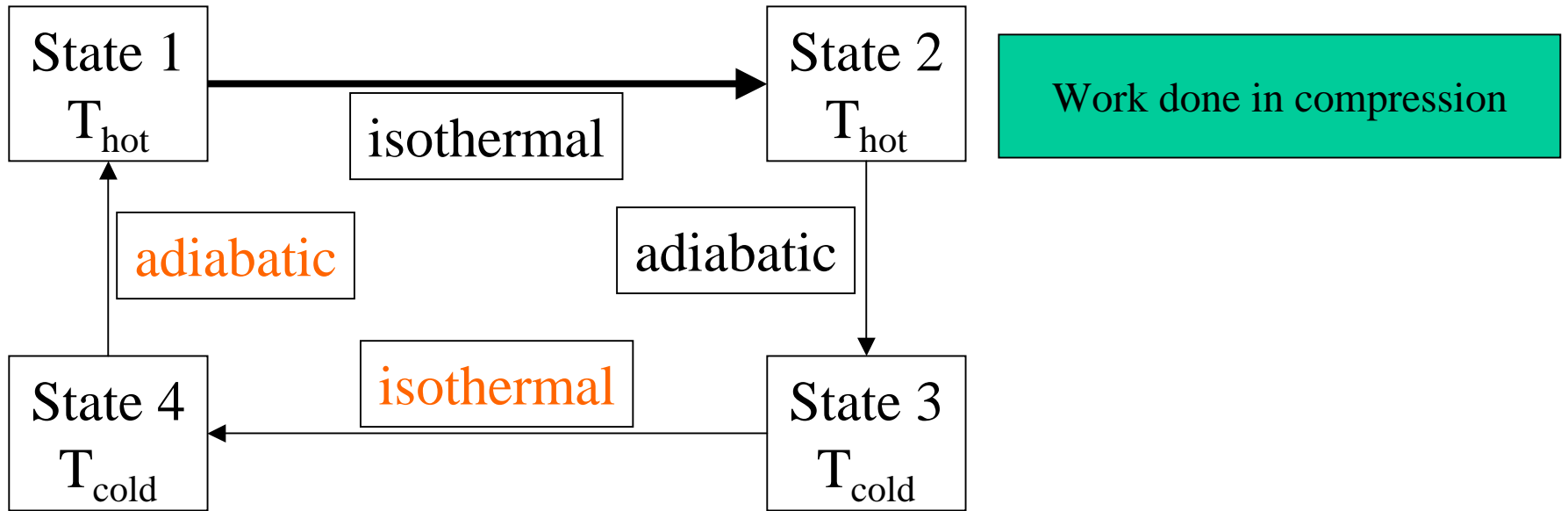
$$w = \Delta E = -C_V \Delta T = -P \Delta V$$

$$C_V dT = -nR T dV$$

$$\int_{T_{\text{hot}}}^{T_{\text{cold}}} \frac{dT}{T} = -nR \int_{V_2}^{V_3} \frac{dV}{V}$$

$$\longrightarrow C_v \ln\left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right) = -nR \ln \frac{V_3}{V_2}$$

The Carnot Cycle: Step 3&4



$$q_3 = -w_3 = nRT_{\text{cold}} \ln(V_4 / V_3)$$
$$q_4 = 0, w_4 = C_V \Delta T$$

The Carnot Cycle: Summary

	Step1	Step2	Step3	Step4
w	$-nRT_{\text{hot}} \ln(V_2/V_1)$	$-C_V \Delta T$	$-nRT_{\text{cold}} \ln(V_4/V_3)$	$C_V \Delta T$
q	-w	0	-w	0
ΔE	0	w	0	w

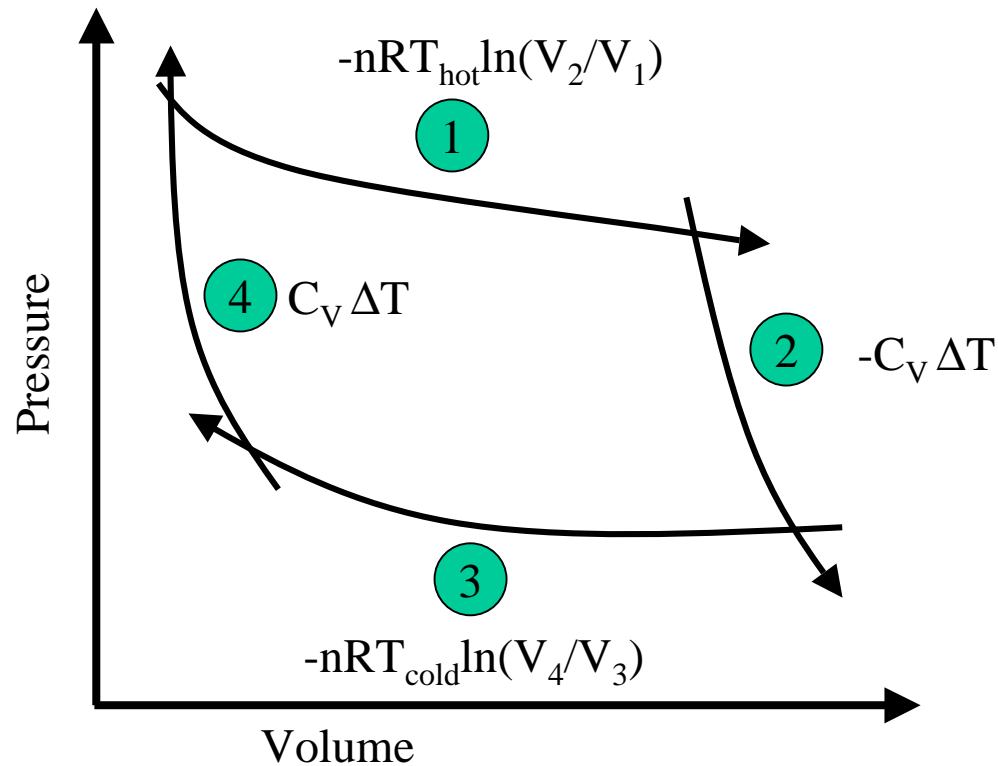
$$C_v \ln\left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right) = -nR \ln \frac{V_3}{V_2}$$

$$w_1 + w_2 + w_3 + w_4 = -nRT_{\text{hot}} \ln(V_2/V_1) - nRT_{\text{cold}} \ln(V_4/V_3)$$

$$q_1 + q_2 + q_3 + q_4 = nRT_{\text{hot}} \ln(V_2/V_1) + nRT_{\text{cold}} \ln(V_4/V_3)$$

$$q = -w$$

The Carnot Cycle: PV Work Diagram



The Carnot Cycle: Efficiency

The efficiency of a heat engine is simply

$$\text{total work accomplished} / \text{total fuel (heat) input}$$

The heat is input only from the hot reservoir so

$$\text{efficiency} = \varepsilon = -w/q_{\text{hot}}$$

So we get two expressions for efficiency:

$$1) \quad \varepsilon = (q_{\text{hot}} + q_{\text{cold}})/q_{\text{ho}} = 1 + q_{\text{cold}}/q_{\text{hot}}$$

and

$$2) \quad \varepsilon = 1 + nRT_{\text{cold}} \ln(V_4/V_3) / nRT_{\text{hot}} \ln(V_2/V_1) = 1 + (T_{\text{cold}}/T_{\text{hot}})(\ln(V_4/V_3)/\ln(V_2/V_1))$$

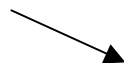
$$\epsilon = 1 + nRT_{\text{cold}} \ln(V_4/V_3) / nRT_{\text{hot}} \ln(V_2/V_1) = 1 + (T_{\text{cold}}/T_{\text{hot}})(\ln(V_4/V_3)/\ln(V_2/V_1))$$

Well, this second expression is rather complicated-- but we have a relationship for the volumes in this process:

$$C_v \ln\left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right) = -nR \ln \frac{V_3}{V_2}$$



$$T_{\text{hot}}^{C_v/nR} V_2 = T_{\text{cold}}^{C_v/nR} V_3$$



$$\frac{V_2}{V_3} = \frac{V_1}{V_4}$$

$$C_v \ln\left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right) = -nR \ln \frac{V_1}{V_4}$$



$$T_{\text{hot}}^{C_v/nR} V_1 = T_{\text{cold}}^{C_v/nR} V_2$$



Rearranging and plugging it in to the first equation on the page:

$$\epsilon = 1 - (T_{\text{cold}}/T_{\text{hot}})$$



$$\varepsilon = 1 - (T_{\text{cold}}/T_{\text{hot}}) = 1 + (q_{\text{cold}}/q_{\text{hot}})$$

100% efficiency is only achieved when

$$T_{\text{cold}}=0 \text{ and } T_{\text{hot}}=\infty$$

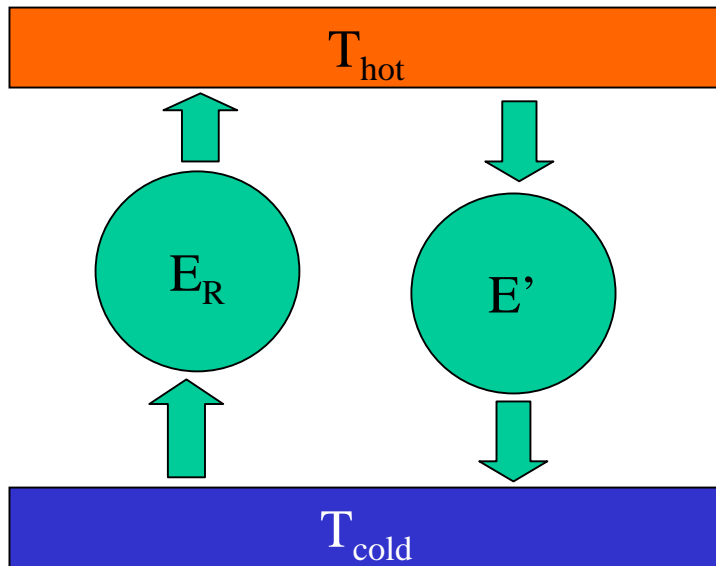
Practical impossibilities.

(Foreshadowing the Third Law)

Can we construct an engine more efficient than this one?

Impossible Machines

Consider two engines E_R and E' operating between the same two reservoirs:



Can the efficiencies of these two engines be different?

We operate E_R in *reverse*.

We couple the operation of the two engines.

We know:

$$w_R = q_{\text{hot}} + q_{\text{cold}} \text{ (forward direction)}$$

$$w' = q'_{\text{hot}} + q'_{\text{cold}}$$

The composite engine then has a total work

$$W = w' - w_R$$

Let's composite the engines so that there is no work on the surroundings:

$$w' = w_R$$

which implies

$$q_{\text{hot}} - q'_{\text{hot}} = -(q_{\text{cold}} + q'_{\text{cold}})$$

Impossible Machines

Can the efficiencies of these two engines be different?

Let's assume $\epsilon' > \epsilon_R$:

$$w'/q'_{\text{hot}} > w_R/q_{\text{hot}}$$

But $w' = w_R$ so

$$q'_{\text{hot}} < q_{\text{hot}}$$

In other words, the heat withdrawn from the hot reservoir is negative!

From above, we also so that this implies that the heat withdrawn from cold reservoir is positive!

Without doing any work we extract heat from the cold reservoir and place it in the hot reservoir!

What was our error?

The Carnot Cycle: Noticing state functions

Assumptions in our proof:

1) The first law:

Experimentally proven.

2) $w' = w_R$

A fully practical assumption

3) $\epsilon' > \epsilon_R$

Hmmmmmm.

That was a bad one...so $\epsilon' \leq \epsilon_R$

Now we assumed that E' was *any engine*, whereas, E_R was *reversible*.

So every engine is either of equal or less efficiency than a reversible engine

(For the same two reservoirs)

The Carnot Cycle: Noticing state functions

Now--- we have this interesting relationship between temperature and heat for these systems:

$$\varepsilon = 1 - (T_{\text{cold}}/T_{\text{hot}}) = 1 + (q_{\text{cold}}/q_{\text{hot}})$$

What Carnot noticed was that there was an implied state function here!

$$(q_{\text{hot}}/T_{\text{hot}}) = -(q_{\text{cold}}/T_{\text{cold}})$$

or

$$(q_{\text{hot}}/T_{\text{hot}}) + (q_{\text{cold}}/T_{\text{cold}}) = 0$$

This can also be written:

$$\oint_{\text{rev}} \frac{dq_{\text{rev}}}{dT} = 0$$

This is a state function! Clausius called it the Entropy, S.



Non-Conservation of Entropy

The question arose, is entropy conserved? After all, energy is.

But a great deal of experience indicated that:

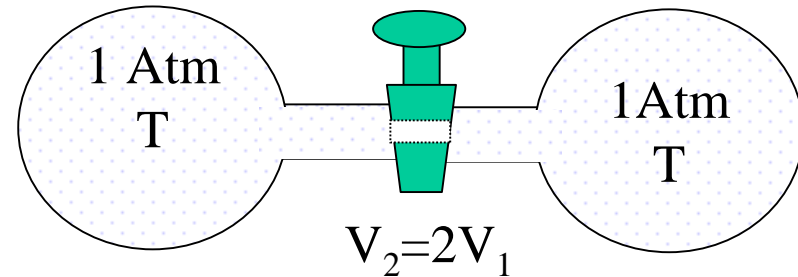
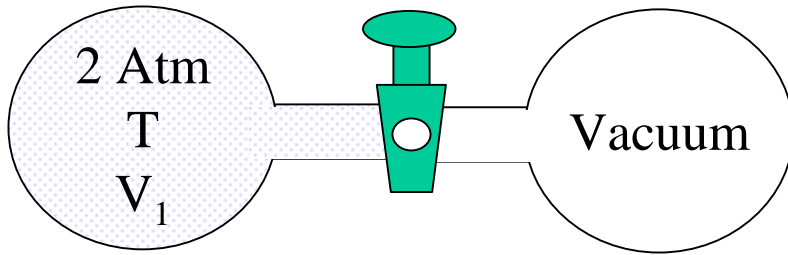
$$\Delta S(\text{system}) + \Delta S(\text{surroundings}) \geq 0$$

This is the *Second Law of Thermodynamics*.

- Heat never spontaneously flows from a cold body to a hot one.
- A cyclic process can never remove heat from a hot body and achieve complete conversion into work

Let's consider a particular case.

Non-Conservation of Entropy



Two cases of expansion of an ideal gas:

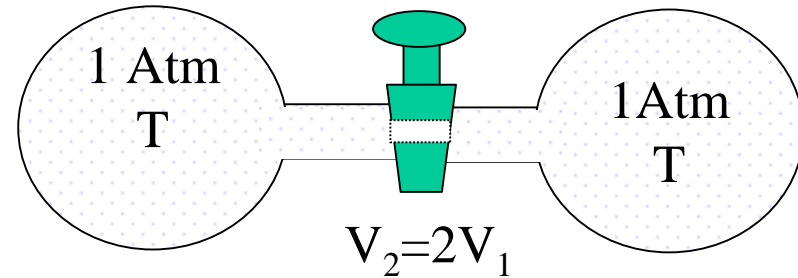
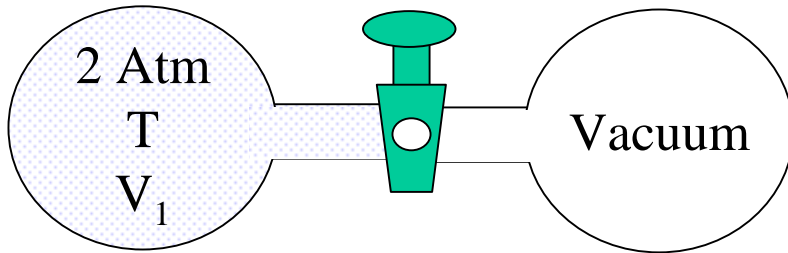
- 1) Expansion in to a vacuum.
- 2) Reversible expansion

(1) $w=0$, $\Delta E=0$, $q_{\text{irreversible}}=0$

$\Delta S(\text{surroundings})=0$

To calculate $\Delta S(\text{system})$ we look to the second process (they must be the same).

Non-Conservation of Entropy



In the second process we follow an isothermal, reversible path.

We know that $\Delta E = 0$ and

$$w = - \int_{V_1}^{V_2} P dV = -RT \ln\left(\frac{V_2}{V_1}\right) = -RT \ln(2)$$

Now... $q_{\text{rev}} = \Delta E - w = RT \ln(2)$ so

$$\Delta S(\text{system}) = q_{\text{rev}}/T = R \ln(2)$$

Thus for the total irreversible process

$$\Delta S = 0 + R \ln(2) > 0$$

Non-Conservation of Entropy

For the reversible process we've already calculated

$$q_{\text{rev}} = RT \ln(2)$$

$$\Delta S(\text{system}) = q_{\text{rev}}/T = R \ln(2)$$

Since the process is reversible-- all the heat must be transferred from the surroundings.

One way to make sure this is reversible is to make sure the outside temperature is only differentially hotter.

$$\Delta S(\text{surroundings}) = -q_{\text{rev}}/T$$

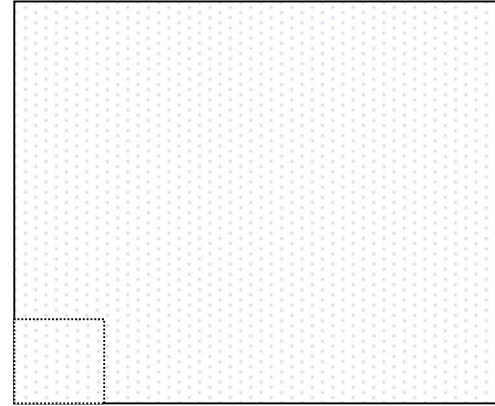
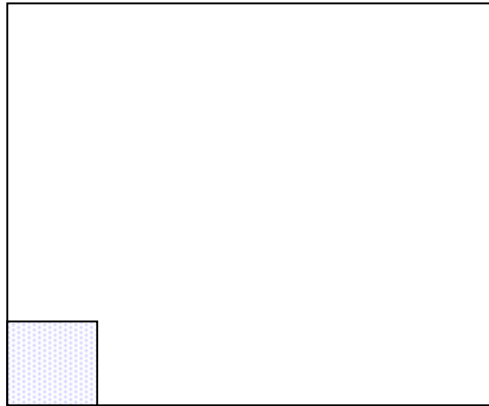
$$\Delta S(\text{total}) = 0$$

Disorder and the relationship to entropy



Ludwig Boltzmann
c. 1875

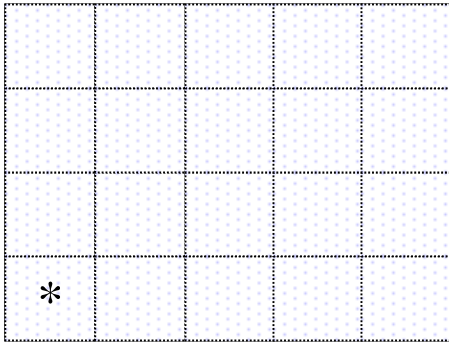
It turns out that disorder and entropy are intimately related.



We start out by considering the spontaneity of this process.

Why doesn't the gas spontaneously reappear back in the box?

Disorder and the relationship to entropy



Let's break the box into N cells and consider the gas to be an ideal gas composed of M molecules.

We ask: What is the probability that M molecules will be in the box labeled '*'

This obviously depends on both M and N. We assume $N > M$ for this problem.

Number of ways of distributing M indistinguishable balls in N boxes is simply:

$$\Omega = N^M / M!$$

Boltzmann noted that an entropy could be defined as

$$S = k \ln(\Omega) = R \ln(\Omega) / N_A$$

There are a number of reasons this is a good definition. One is it connects to thermodynamics.

Disorder and the relationship to entropy

So for a given state we have

$$S = k \ln(\Omega) = R \ln(\Omega)/N_A = R \ln(N^M/M!)/N_A$$

Let's say we change state by increasing the volume. Well, for the same sized cells, N increases to N' .

$$\begin{aligned} S' - S &= (R/N_A) (\ln(N'^M/M!) - \ln(N^M/M!)) \\ &= (R/N_A) \ln(N'^M/N^M) \end{aligned}$$

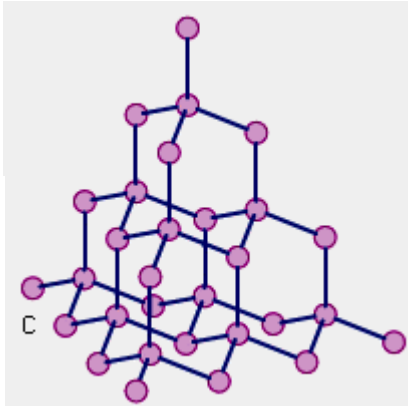
So

$$\Delta S = (R/N_A) \ln(N'^M/N^M) = M (R/N_A) \ln(N'/N)$$

And since N is proportional to volume:

$$\Delta S = M (R/N_A) \ln(V2/V1)$$

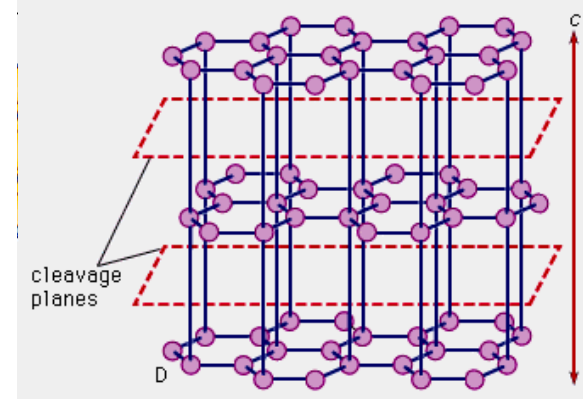
Entropy of Materials



Diamond

$$S^{\circ}_{298} = 2.4 \text{ J/K}$$

Why does graphite have more entropy than diamond?



Graphite

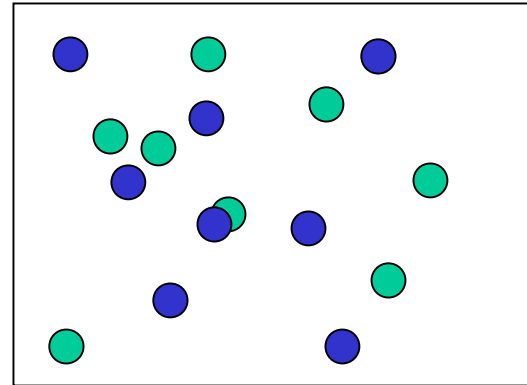
$$S^{\circ}_{298} = 5.7 \text{ J/K}$$

How about water in its different phases:

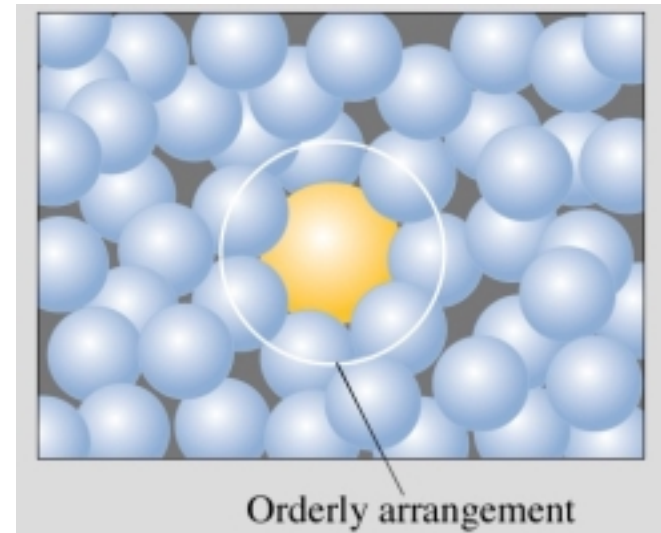
	S°_{298} (J/K mol)
$\text{H}_2\text{O}(\text{s,ice})$	44.3
$\text{H}_2\text{O}(\text{l})$	69.91
$\text{H}_2\text{O}(\text{g})$	188.72

Entropy and Mixing

What happens when you mix two ideal gases?

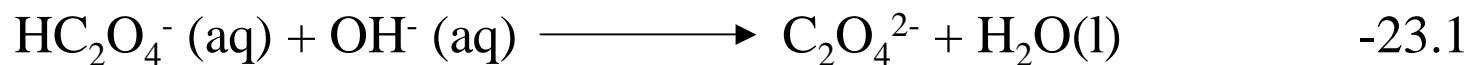


What happens when you solvate a molecule?





Entropy and Chemical Reactions

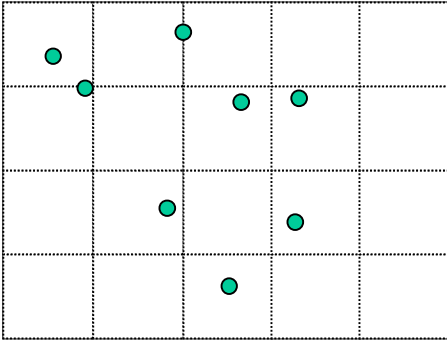


It's hard to predict the change in entropy without considering solvent effects

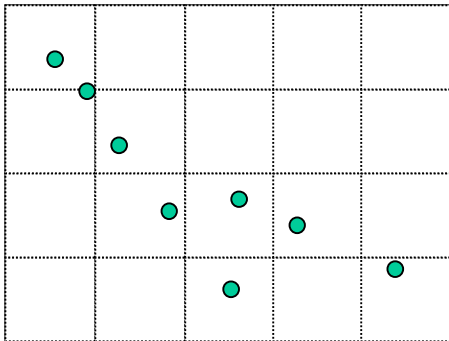
Calculation of ΔS for a reaction is similar to that for enthalpy.

Entropies of elements are **not** zero though.

Fluctuations



All the previous arguments relate to processes involving large numbers of molecules averaged over long periods of time.



When the system is small and observation time is short, then fluctuations around the “maximum” entropy solution can be found.

Homework: For Next WEEK!

This is an early announcement for the homework for Monday. It might be changed slightly. But its good practice for the exam.

1-3) TSW 3.1, 3.3, 3.7

4) Sketch all possible arrangements of

a) Two balls in six cells

b) Four balls in six cells

c) For each of A and B, what is the probability that half the balls will be in the first three cells and half in the second three?

Assume the balls are indistinguishable and the cells may contain only one ball.